MICROCRYSTALLINE CELLULOSE FROM COTTON RAGS (WASTE FROM GARMENT AND HOSIERY INDUSTRIES)

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ABSTRACT

Cellulose is the most abundant organic compound with the formula $(C_6H_{10}O_5)_n$. On our globe, approximately 10^{15} Kg/yr is synthesized and degraded and is found in plenty in nature in the form of cotton, hemp, jute, flax etc. A good percentage of wood also consists of cellulose.

Waste management is one of the biggest problems faced by the human beings in industry as well as domestically. Garment and hosiery industries are having the abundant waste of the cotton rags, cuttings etc. during the manufacturing of garments. As cotton is having highest percentages (87 to 96 %) of cellulose, it can be used for manufacturing of value added products like microcrystalline cellulose (MCC).

Microcrystalline cellulose (MCC) is very important product in pharmaceutical, food, cosmetic and other industries. It can be derived by number of processes like reactive extrusion process, enzyme mediated process, the steam explosion process and acid hydrolysis process etc. Out of these processes, the acid hydrolysis process is used in this study because it requires shorter reaction time than other processes. It can be made by a continuous process rather than a batch-type process and it uses limited amount of acid and produces small particles of microcrystalline cellulose.

In this study, MCC was produced from cotton rags, produced in large quantities in garment and hosiery industries. It was characterized through various techniques like infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The results obtained show that the prepared sample has similar crystallinity, lower particle size, good thermal stability and less residue content.

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INTRODUCTION

Cellulose is the most abundant organic compound with the formula $(C_6H_{10}O_5)_n$. On globe, approximately 10^{15} Kg/yr is synthesized and degraded and it is found in plenty in nature in the form of cotton, hemp, jute, flax etc. A good percentage of wood also consists of cellulose. Cellulose has an extremely high degree of crystallinity and this is due to the formation of several hydrogen bonds originating from its hydroxyl groups. Its high stereo-regularity is also a contributory factor for its high crystallinity. Pure cellulose, also known as α- cellulose, is a material insoluble in 17.5 % NaOH. β-cellulose and γ-cellulose are not true cellulose. β–Cellulose beloved to be degraded. It has low degree of polymerization cellulose and is insoluble in 17.5 % NaOH; γ-Cellulose is completely soluble at any pH and is thought to be hemicelluloses such as xylans, mannas, galactans etc.

MCC is obtained on industrial scale from wood and cotton cellulose, but also obtained from materials such as soyabean husk (Nelson Yoshio Uesu, Edgardo Alfonso Go´mez Pineda, Ana Adelina Winkler Hechenleitner, 2000), water hyacinth (Gaonkar and Kulkarni, 1987), coconut shells (Gaonkar and Kulkarni, 1989), sugar cane bagasse (Padmadisastra and Gonda, 1989; Shah et al., 1993) and jute (Abdullah, 1991).

In the present work, MCC was prepared from cotton rags. It was characterized through infrared spectroscopy (FTIR) and X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Reagents and chemicals

Cotton rags were obtained from local market shop of 100 % cotton. Hydrochloric acid and iodine solutions were of analytical reagent grade supplied by S. D. Fine Chemicals (INDIA). These chemical were used as received without further purification.

MCC preparation

In this experiment, 2.5 N hydrochloric acid (HCl) was used. Cotton rags are taken (5 g). The solid to liquid ratio was kept 1 : 20 i. e. for one gram of cotton rags and the amount of HCl solution is 20 mL. In this case, 5 g of cotton rags with 100 mL of HCl solution was processed.

Initially, 100 mL HCl solution of 2.5 N was taken in a 250 mL flask and kept it in a heating mental. The temperature of heating mental was kept constant at 85ºC and stirring of HCl solution started. After getting the 85ºC temperature of HCl solution, cotton rags were added in the solution slowly with continuous stirring. After complete addition of cotton rags, the mixture of cotton rags and HCl solution ws kept under continuous stirring for one and half hours. After confirming the complete depolymerization of cotton rags, the heating and stirring was stopped and the mixture was kept for cooling.

After getting the mixture at room temperature, it was neutralized with water to get the neutral pH of the wash water. Then this mixture was filtered with the Watmann 42 filter paper separating the microcrystalline cellulose (MCC) and neutral water. Then this microcrystalline cellulose was again washed with acetone to remove traces of water present. Again filtration was done to separate acetone and microcrystalline cellulose. After filtration, the microcrystalline cellulose was kept for natural drying. After complete drying, the microcrystalline cellulose was weighted (4 g).

Purity and identification test

Purity test of MCC was done by taking 1 mg of sample in 1 mL of phosphoric acid and it was heated on a water bath for 30 minutes. Then 4 mL of 0.2 % (w/v) solution of catechol in phosphoric acid was added and it was again heated for further 30 minutes. A red colour was produced, which shows that prepared MCC is pure.

Identification test of starch and dextrin was done by mixing 0.1 g of MCC with 5 mL of water with vigorous shaking and adding three drops of iodine solution. A brownish-red colour was observed, which confirms the presence of starch and dextrin in prepared MCC.

MCC analysis

All analysis has been done at GIST (Gharda Institute of Science and Technology) and Quality Assurance Department of Gharda Industries Limited, B-27/29 MIDC, Dombivli (E) – 421203.Dist. Thane. Maharashtra State (INDIA).

MCC sample was analyzed by FTIR using Jasco FT/IR, Fourier Transform Infrared Spectrometer, Model : - FT/IR – 410, Serial No. : - A000360585, Power : - A/C 220 V-50/60 H_z – 120 W, Project : - Class I, Made in Japan. For FTIR scan, KBr pellets containing 2 % (8.5 mg MCC + 398 mg KBr were mixed together and pressed into a tablet at 200 kg/cm^2) of the sample was prepared. Spectra in the range of 400 – 4000 cm^{-1} was

obtained with a resolution of 2 cm^{-1} and the signal was accumulated from 100 scans. For structural changes of MCC sample evaluation, three ratios of peak areas were analyzed : the paracrystalline regularity index ($\phi = A_{1370}/A_{897}$), which can be related with degree of ordering of the largest macromolecules (Ershov and Klimentov, 1984) and the $I_1 = A_{1430}/A_{897}$ and $I_2 = A_{1370}/A_{2900}$ indices, which have been proposed as sensible to cellulose type I and type I and II crystallinity, respectively (Nelson and O'Connor, 1964).

The crystal structure MCC samples were studied by X-ray diffractometer (D/MAX-1200, Rigaku, Japan) and the diffraction angle 2θ was from 6º to 40º. Profile analysis was carried out with peak fitting program using Gaussian line shapes to determine the crystallinity of samples. The crystallinity was taken at the ratio of the sum of areas under the crystalline diffraction peaks to the total area under the curve between $2\theta = 6º$ and 40º. Approximately 150 mg MCC sample of 240 mesh size was taken in sample holder. The X-ray diffraction pattern was obtained with Kb-filtered Cu Kα radiation using an X-ray generator (Rigaku RINT2000) at 30 kV, 15 mA. The other specifications are as Divergence slit : Variable, Scattering slit : 4.2 deg. and Receiving slit : 0.3 mm, Scan mode : continuous, Scan speed : 1.000 deg. /min., Sampling width : 0.01 deg., Scan axis : $2\theta/\theta$, Scan range : 6.00 -> 40.00 deg., Theta offset : 0 deg., Repeat count : 1 and irradiated width : 11.49 mm.

Thermogravimetric analysis (TGA 2050, TA) was carried out to determine the thermal stability of samples at nitrogen current of 10 mL min^{-1}. The sample weight was taken as 13.910 mg and it was heated from 50º to 800º C at a heating rate of 10ºC/min. Derivative TG (DTG) curves expressed the weight-loss rate as a function of time. Profile analysis of DTG curve was done with peak fitting program of Peakfit Software using Beta line shape. The baseline was corrected by non-parametric model with 0.5% tolerance and the deconvolution Peakfit model was used to fit the DTG data.

RESULTS AND DISCUSSION

The FTIR spectrum, X-ray diffraction curve, thermogravimetric analysis (TGA) and derivative TG (DTG) curve of MCC obtained from cotton rags are shown in the Figs. 1– 4.

The FTIR spectrum (Fig. 1) is very similar with that of commercial MCC and is characteristic of cellulose type I. The ϕ, I_1 and I_2 parameters obtained were 2.52, 7.66 and 0.11 for the prepared MCC, respectively from cotton rags. This result indicates similar crystallinities as that of commercial MCC.

The X-ray diffractometer was used to investigate the crystalline structure of sample and the X-ray curve of prepared sample is shown in Fig 2.From the X-ray curve, it was clearly observed that the X-ray diffraction patterns of prepared samples and commercial MCC are similar. This observation indicated that the crystalline structure of cellulose I of MCC has been maintained after hydrolysis with hydrochloric acid at higher temperature up to 86ºC. Also the degree of crystallinity is nearer to commercial MCC having 83% and of prepared is 81%.
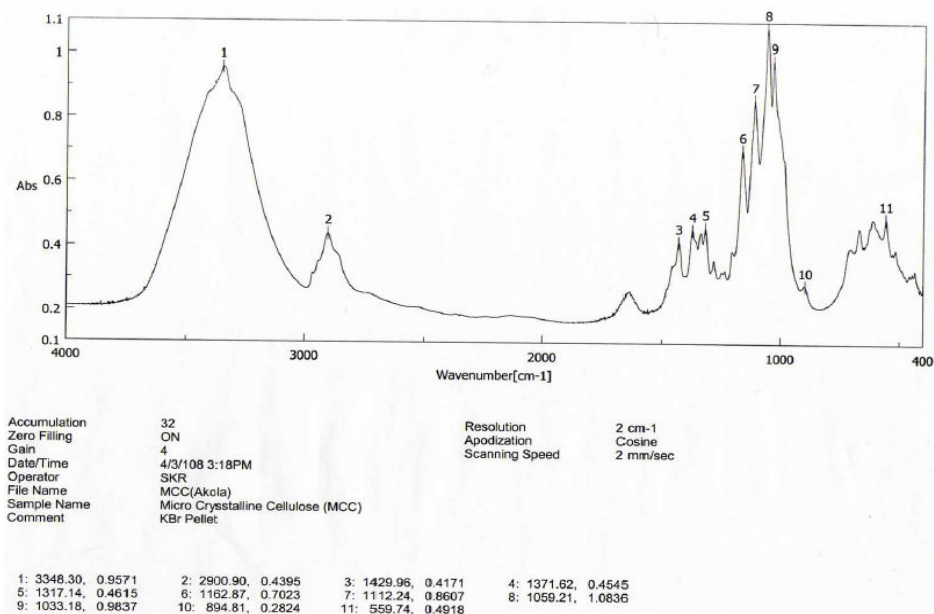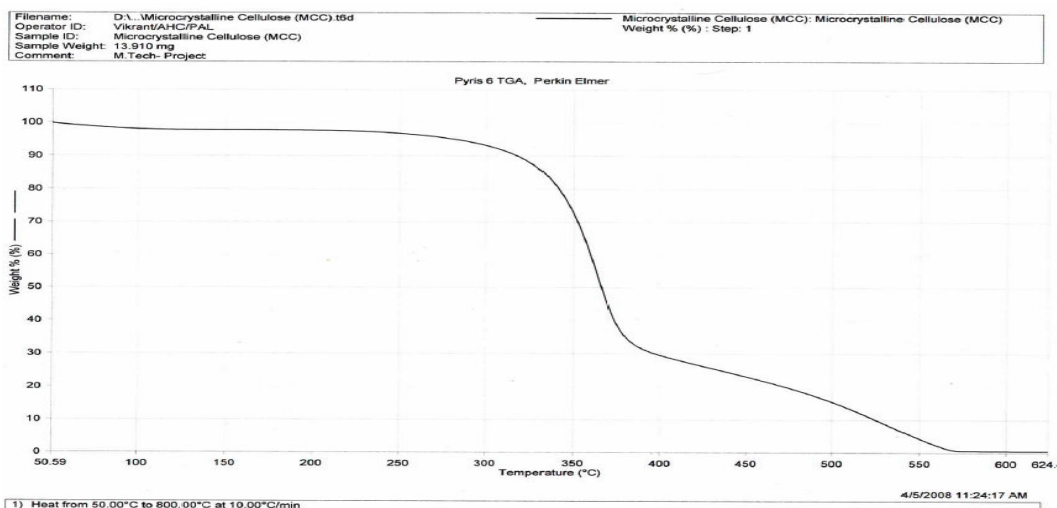

Fig. 1.Infrared (FTIR) spectra of the prepared microcrystalline cellulose (MCC) from cotton rags

In Fig. 3, a thermogravimetric (TGA) curve of the prepared microcrystalline cellulose (MCC) from cotton rags is shown. It shows that the MCC sample undergoes mass loss from 50ºC to 800ºC. The nature of the curve is very much similar to that of commercial MCC. The thermal decomposition is initiated near 270ºC, which is very similar to the commercial MCC. The weight loss (Fig. 4) at 100ºC is only 1.803% and at 250ºC is 3.110 %; it shows the prepared MCC from cotton rags is good temperature resistant. The initial degradation temperature of the prepared MCC is 334.96ºC; it shows a good thermal stability. The total weight loss found at 600ºC is 99.402 % : which shows that only 0.598 % [@ 0.6 %] is the residue present in the prepared MCC. These results indicate similar crystallinities for both the MCC samples i. e. for commercial and prepared from cotton rags.
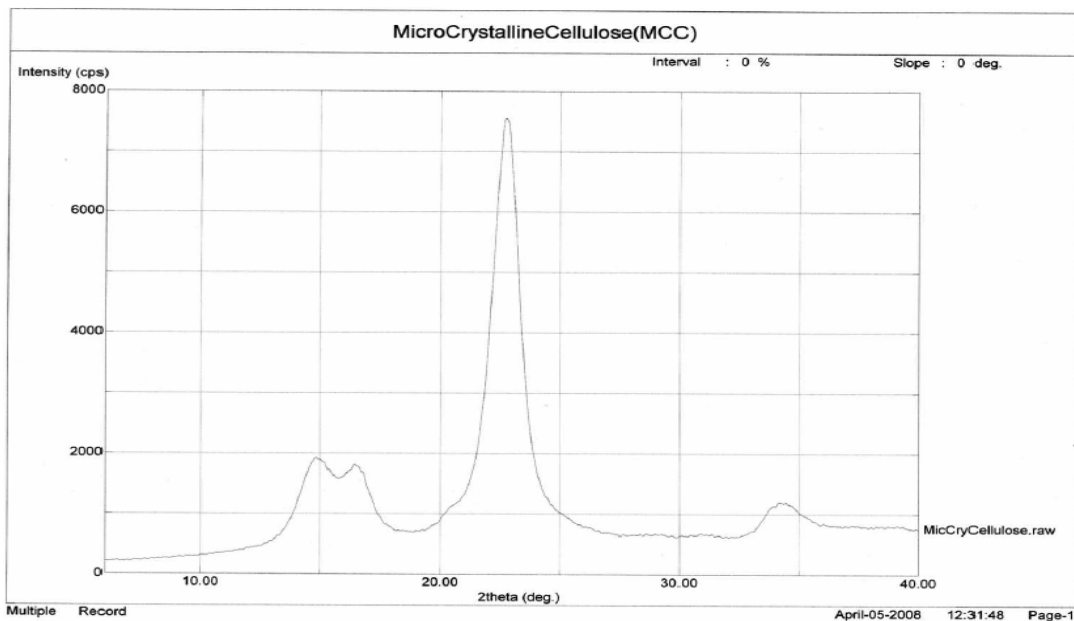
Fig. 2.The X-ray curve of the prepared microcrystalline cellulose (MCC) from cotton rags.

Fig. 3.Thermogravimetric analysis (TGA) curves of the prepared microcrystalline cellulose (MCC) from cotton rags.
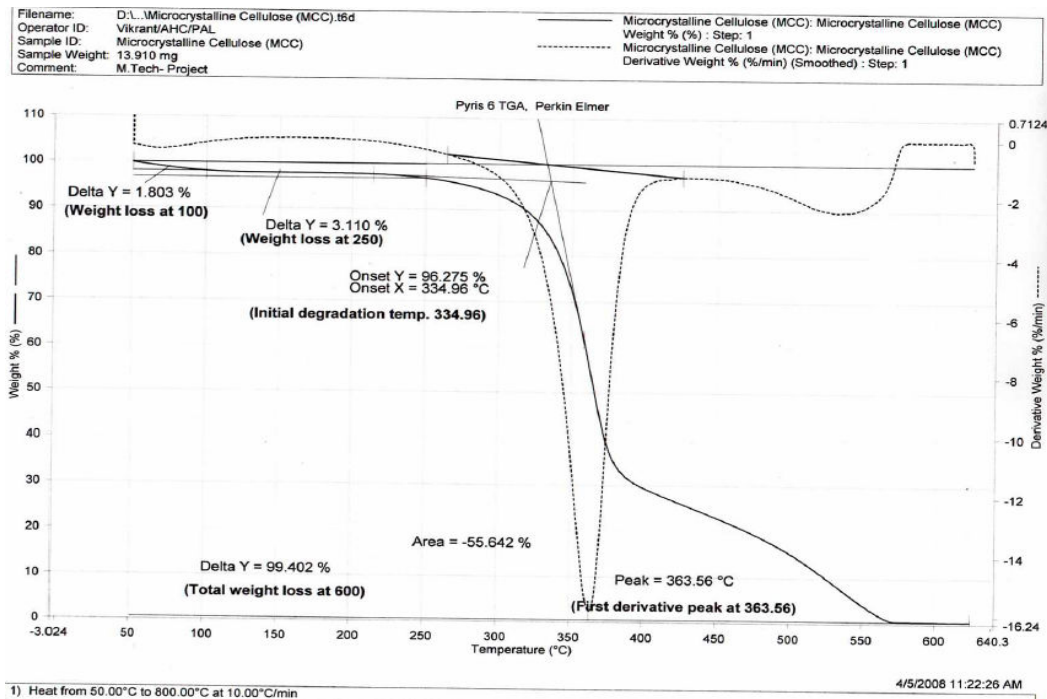
Fig. 4. Derivative TG (DTG) curve of the prepared microcrystalline cellulose (MCC) from cotton rags

The derivative TG (DTG) curve of the prepared MCC from cotton rags is shown in the Fig. 4. The first derivative peak is observed at 363.56ºC. The degradation i. e. thermal decomposition occurred within a wider temperature range and showed two well separated pyrolysis processes. One process occurred between 265ºC and 420ºC and the other between 485ºC and 575ºC. The area of first derivative peak is found 55.642 % of the total.

CONCLUSION

MCC prepared in this work from cotton rags (waste of Garment and Hosiery industries), has properties similar to that of a commercial MCC. The FTIR is same for prepared and commercial MCC, which shows the similar crystallinity. The X-ray curves of prepared MCC from cotton rags and commercial MCC show the same diffraction pattern; which indicates that the crystalline structure of cellulose *I* is not disturbed even it is treated with the hydrochloric acid at higher temperature up to 86ºC. Also the degree of crystallinity is nearer to commercial MCC having 83% and of prepared is 81%. The TGA curve of the prepared and commercial MCC are very similar. The initial degradation

temperature of the prepared MCC is 334.96ºC; it shows a good thermal stability. The total weight loss found at 600ºC is found 99.402 % : which shows that only 0.598 % [@ 0.6 %] is the residue present in the prepared MCC. These results indicate similar crystallinities for both MCC samples i. e. for commercial and prepared from cotton rags.

Residues from annual plants such as sugar cane bagasse, cereal straws, corncobs, cereal husks, etc. are interesting alternatives as cellulose source for several applications. Such materials are renewable and widely available in many regions of the world and are generally burned or disposed for ambient degradation.

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